

SILICON CARBIDE SINTERED BODY MANUFACTURED FROM SILICON CARBIDE
POWDER CONTAINING BORON, SILICON, AND CARBONACEOUS ADDITIVE

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16. Abstract A silicon carbide powder of grain size of 5 mu is mixed with 0.15-0.60 wt.% a mixt. of a boron cpd., e.s. boric acid, boron carbide (B4C), silicon boride (SiB4 or SiB6), aluminum boride, etc., and an aluminum cpd., e.s. aluminum, aluminum oxide, aluminumhydroxide, aluminum carbide, etc. or an aluminum boride (AlB2) alone, in such a proportion that the boron/aluminum atomic ratio in sintered body becomes 0.15-3.0 and also the boron and aluminum contents of the sintered body becomes 0.05-0.25 wt% and 0.05-0.40 wt% respectively, together with a carbonaceous additive to supply enough carbon to convert oxygen accompanying raw materials and additives into carbonmonoxide.					
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(54) Method of Manufacturing Sintered Silicon Carbide

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DETAILED EXPLANATIONS

1. Name of invention: Method of Manufacturing Sintered Silicon Carbide

2. Area Covered by the Present Patent Application

1. A method of manufacturing sintered silicon carbide is characterized by the following features:

To silicon carbide powder, we add sinter-acceleration agents of both boron and aluminum groups whose net amount is 13-60 wt.%. We also mix additives of the carbon group whose amount is sufficient for making carbon monoxide from oxygen contained in the initial material and additives, and also sufficient for fixing silicon produced from the boron and aluminum reaction as carbide, in addition to supplying carbon of 0.1 - 0.3 wt.% of silicon carbide. If necessary, we pulverize it. Then we sinter it in inert gas environment at 1850-2200°C.

2. The method of manufacturing sintered silicon carbide is described in article 1 of the area covered by the patent in which the atomic ratio B/Al of boron and aluminum in a sintered body is 0.15 - 3.0 wt.%.

3. A method of manufacturing sintered silicon carbide is described in Article of of the area covered by the patent, in which the amount of boron sinter-accelerating agent added is the amount for providing boron of 0.05 - 0.25 wt.% in the sintered body, and the amount of aluminum sinter-accelerating agent is such that it supplies aluminum of 0.05-0.40 wt.% in the sintered body.

4. The method of manufacturing sintered silicon carbide is described in Articles 1 and 2 of the area covered by the patent in which the sinter-acceleration agent is AlB_2 alone or AlB_2 and sinter-acceleration agents of the boron group or the aluminum group, or a mixture of AlB_2 and AlB_{12} .

5. The method of manufacturing sintered silicon carbide is described in Articles 1,2,3, and 4 of the area covered by the patent in which the grain diameter of silicon carbide is less than 5 μ .

3. DETAILED EXPLANATION OF INVENTION

The present invention is concerned with an improved manufacturing method of sintered silicon carbide.

Sintered silicon carbide is highly heat resistant, has a small thermal expansion coefficient, and also high density sintered silicon carbide is strong at high temperatures. Thus the material is of interest as construction material at high temperatures.

In the past, the following have been used as methods for manufacturing sintered silicon carbide: (1) To silicon carbide powder with a grain size less than 10μ , an aluminum or aluminum chemical compound of 0.5-5 wt.% is added and sintered at high pressure and temperatures above 1950°C in an inert gas atmosphere (Public Announcement, Patent Announcement 52-6716). (2) To the β -type silicon carbide powder, a boron additive equivalent of boron of 0.3-3.0 wt.% and a carbon additive equivalent of carbon of 0.1-1.0 wt.% are added, and sintered in inert gas atmospheres at 1950 - 2300°C (Public Announcement, Patent Announcement 52-6716).

The present inventors studied these two systems and found that the dissolution limit of aluminum and boron into solid silicon carbide is less than 0.4 wt.% and 0.3 wt.% near 2000°C , at which sintering is usually done. The excess amounts of aluminum and boron remain in the sintered grain and grain boundaries after sintering, and reduce the strength of the sintered body at high temperatures. By adding these two additives within the solid dissolution limits, together with an additive of the carbon group, silicon carbide powder, which is hard to sinter when the amounts of the aluminum and boron additives are within the solid dissolution limit, becomes relatively easy to sinter. They also found a sintered body which does not have different phases in large quantity at the grain boundaries. Based on the discovery, the present invention was accomplished.

In the present invention, sinter-acceleration additives of the boron and aluminum groups of the amounts equivalent to the net amount of 0.15 - 0.60 wt.% of the sintered body and an

additive of the carbon group (which supplies carbon of 0.1-0.5 wt.% required for producing carbon monoxide from oxygen contained in the original material and additives, and also required for fixing silicon produced by the reaction of boron and aluminum and boron and aluminum as carbides) are added to silicon carbide powder, preferably with grain size less than 5μ , and then pulverized and dried if necessary. Then the mixture is sintered at $1850-2200^{\circ}\text{C}$ in an inert gas atmosphere.

There is a variety of silicon carbide polymorphism for the raw material. However, in the present invention, any polymorphism can be used. The grain size of the powder is less than 5μ , preferably less than 2μ . This is because, if the sintering conditions are identical, the density will increase rapidly as the grain size decreases and the specific surface area increases.

Also the amount of metal impurities should be less than 0.5 wt.%, preferably less than 0.4 wt.%.

As a sinter-acceleration agent of the boron group, for example, we have boron, boron carbide (typically B_4C), silicon boride (S_2B_4 or S_2B_6) and aluminum boride (AlB_2 or AlB_{12}). As additives of the aluminum group, we have, for example, aluminum, alumina, aluminum hydroxide, aluminum carbide, and aluminum boride (AlB_2 or AlB_{12}). If aluminum boride is used, it can be used as a sinter-acceleration agent of the boron group as well as of the aluminum group. However, we are not limited to the above chemicals.

The amounts of these additives are preferably such that the net amount of boron and aluminum in a sintered body is 0.15-0.60, or better 0.15-0.40 wt.%, the atomic ratio (B/Al) of boron and aluminum is 0.15-3.0 wt.%, of boron 0.05-0.25 wt.%, aluminum 0.05-0.40 wt.%. These amounts of additives are the net of the amounts added, plus the amounts contained in the raw material if the latter existed as impurities.

If the net amount of boron and aluminum in a sintered body exceeds 0.60 wt.%, a melt of high temperature of $1500-1600^{\circ}\text{C}$ tends to remain even at the sintering temperature. This causes abnormal grain growth and reduces the mechanical strength of the sintered body. If the amount is less than 0.15 wt.%, sintering is poor.

The reason for setting the upper limits of the boron and aluminum additives to 0.25 wt.% and 0.40 wt.%, respectively, is that, if the amounts are greater, the excess amounts give non-uniform residues of high concentration at the grain boundaries.

In the present invention, if both sinter-acceleration additives of the boron and aluminum groups are added simultaneously, a melt of high temperature is formed at 1500-1600°C. This is a special phenomenon which occurs if both of the sinter-acceleration additives are added simultaneously. This is not observed if the boron or aluminum additive is added separately.

Formation of the high temperature melt is harmful to sintering, if the amount is large. However, if the amounts of the additives are those given by the present invention, this contributes to uniform dispersion of the additives in the process of raising the temperature for sintering. This appears to be the reason for sintering with the amounts of the additives being less than those in the conventional method.

In the present invention, additives of the carbon group perform the following three functions:

(1) Oxygen contained in the oxidized surface of silicon carbide powder and in the additives is partly removed as vapor at high temperatures. The remaining oxygen is removed from the system as carbon monoxide.

(2) It reacts with silicon, which existed as free silicon in silicon carbide or is formed at high temperatures in the above process (1), or in the process of dissolving the additives or in silicon monoxide vapor, boron, and aluminum, to fix them as carbides.

(3) A part of the residue in the sintering process stays at the grain boundary and suppresses migration of the grain boundary and grain growth.

As additives of the carbon group, we have, for example, graphite and fine powder of carbon. However, in order to uniformly disperse carbon, it is desirable to have additives of organic compounds such as sugars and a furfuryl alcohol-formaldehyde

mixture, or a phenol-formaldehyde mixture which can dissolve in water or organic solvents and produce free carbon when heated to 400-1000°C in a non-oxidizing atmosphere.

The proper amount of the additive is the net amount which removes oxygen contained in silicon carbide and other additives as carbon monoxide, and also fixes boron, aluminum, and silicon created by chemical reactions as carbides, and supplies carbon of 0.1 - 1.0 wt.%, or preferably 0.1-0.5 wt.% of silicon carbide.

If the amount of the additive is more than 1.0 wt.% of silicon carbide, excess carbon remains in the sintered body and reduces the mechanical qualities and resistance to oxidization, which is undesirable.

Also if the amount is less than 0.1 wt.%, a smooth sintering process is hindered.

These silicon carbide and additives are pulverized and mixed in a mixer which consists of a net mill whose main passage is lined with sintered silicon carbide, a ball mill whose inner wall is lined with sintered silicon carbide, and a sintered silicon carbide ball, or a mixer whose interior is lined with resin, in order to avoid the intrusion of impurities.

If additives of the carbon group are organic compounds described earlier, we can mix solutions of these organic compounds in water or organic solvents and mix the pulverized mixtures of other components in the solution, to provide uniform dispersion. Then, we dry the mixture. In this case, we heat the resultant mixture at 400 - 1000°C in a non-oxidizing atmosphere, decompose the organic compound to create free carbons, and then sinter the mixture. An alternate method is to decompose the above organic compounds in the sintering process in an inert gas such as argon and helium of one atmospheric pressure or less. Then, we continue the sintering. In this case, besides the organic compounds which produce free carbons, we can use, whenever necessary, an organic substance combiner, such as polyvinyl butylal and polyvinyl acrylate (together with plasticity agents if needed). Then we can

easily shape the material in the cooling interval.

As described earlier, in the present invention we can sinter by using a small amount of sinter-acceleration agent by the simultaneous use of sinter-acceleration agents of the boron and aluminum groups. This also causes more uniform dispersion, and by adding a proper amount of additives of the carbon group, we can remove oxygen in the sintered body. Due to this, sinter-acceleration agents do not form different phases in the sintered body. The agents are dispersed in SiO_2 , and the sintered body has superior properties, such as high strength and anti-oxidation properties, even at high temperatures.

Example 1.

We mixed a fine powder of silica and carbon black at the molar ratio of 1:4, and heated the mixture in an argon atmosphere at 1800°C for 1 hour inside a graphite container. Then we oxidized the reaction product at 600°C to remove residual carbon. We treated it with nitric acid fluoride to remove free silicon and oxides, rinsed in water and dried.

The product contained a slight amount of 6H, but was mostly of the β -type. It was a fine powder of silicon carbide. The grain diameter was less than 2μ , and the specific surface area was $5.2 \text{ m}^2/\text{g}$. Results of the chemical analysis of metal impurities in this fine powder are shown below.

Quantitative Analysis Weight %

Fe	0.02	(color comparison)
Ag	0.04	(color comparison)
O	0.12	(radiation analysis)

Fluorescence spectroscopic analysis

Al	++	Si	+
Al	++	Ca	+
Fe	++	Mg	+
Si	+	Mn	+
Ti	+		

(Note) The signs indicates trace + detection and + - presence of a small amount.

We added to this fine powder of aluminum boride (AlB_2) of 0.36 wt.% furfuryl alcohol and formaldehyde (it showed carbon residue of 25wt% at $1000^{\circ}C$ and in the argon environment of one atmosphere pressure) of 3 wt% and ethanol of 20 wt%.

We placed this in a ball mill whose inner wall was lined with sintered silicon carbide, and pulverized, mixed and dried it to obtain the mixture of fine powder.

We placed this mixed powder in a boat made of silicon carbide, raised its temperature to $800^{\circ}C$ in an argon atmosphere. In this way, we carbonized the condensed body of furfuryl alcohol and formaldehyde. After cooling, we sintered this for 10 minutes in an argon atmosphere, of 500 kg/cm^2 pressure at $2000^{\circ}C$, using graphite.

The sintered body is silicon carbide powder of average grain size $10 \sim 15 \mu$. Results of electron beam x-ray microanalysis showed that no presence of boron and aluminum was detected at the grain boundaries. The properties of this sintered body are shown below.

Apparent Density	$3.128/\text{cm}^3$
Pore Ratio *	<1%
Bending Strength (room Temperature) **	

Impurities***

Fe	0.02 wt%
Al	0.23 4
B	0.15 6

Polymorphism $\beta > 6H \sim 4H$

* By optical microscope

** Three point bending, Spran 30.

*** By color comparison.

Example 2.

We placed silicon carbide for industrial use of the second class green (commercially available) and black (both grain sizes are less than 200 mesh) in a jet mill whose main powder path was made of steel. We repeatedly pulverized it by separating the product according to grain size with an air flow. We rinsed it in water and obtained fine powder of grain size less than 1.3μ . We oxidized this fine powder in oxygen flow at 600°C and treated it with hydrochloric acid and nitric acid fluoride. Results of analysis of this product are shown below:

Polymorphism	Impurities (wt%)
green	Fe 0.02 0.02 0.12
black	Al 0.23 0.02 0.22

We added to this fine powder sinter acceleration agents of the boron aluminum and carbon groups in the condition described below. The properties of the sintered body are as follows:

	<u>Green</u>	<u>BLACK</u>
Powder specific surface area m^2/g	4.3	5.1
Additive of boron group and its amount	B fine powder, 0.15 wt%	same
Additive of aluminum group and its amount	Al_2O_3 , 0.35 wt%	same
Additive of carbon group (dispersion medium) and its amount	cane sugar (water) 2.5 wt%	same, 2.1 wt%
Preliminary baking	Argon 600°C	same
Environment, temperature	Argon 2000°C	same
Pressure of sintering	300 kg/cm^2	same

	<u>GREEN</u>	<u>BLACK</u>
Sintering time	10 minutes	same
Average grain size of sintered body	5 ~ 10 μ	5~10 μ
Apparent density	3.16 g/cm ³	3.18 g/cm ³
pore ratio	<0.5%	0
Bending strength (room temperature)	51kg/mm ²	53 Kg/mm ²
Polymorphism	6H>4H>15R	4H~6H>15R

(Note) The above amounts of the additive are given in wt% with respect to silicon carbide powder. Also, the carbon residue rate of cane sugar at 600°C in argon flow is 23 wt%.

Results of electron beam x-ray microanalysis of the above sintered body did not result in segregation of aluminum and boron in the sintered body.

The material "black" contained initially aluminum of 0.22 wt%. Therefore, we did not add additives of the aluminum group.

Example 3.

We mixed fine shapeless silica powder of high quality and carbon black at the molar ratio of 1.4 by using a ball mill made by Merro. We heated the mixture in an argon environment at atmospheric pressure at 1900°C for 30 minutes. Then we held it at 2300°C for 10 hours. We cooled it and removed free carbon by oxidation. Next, we pulverized it by a jet mill as described in example 1, refined and obtained fine powder of silicon carbide. The composition and results of the analysis are shown below:

Specific surface area	4.9 m ² /g
Composition (wt%)	6H 80%, 15R 10%, β 10%
Impurities (wt%)	Fe 0.02%, O - 0.14%

We added sinter acceleration additives of the boron, aluminum and carbon groups under the condition described below, and did preliminary baking and sintering under the following conditions given below. Properties of the sintered body are given below.

Sinter acceleration agents of boron group and amount	B fine powder	0.15 wt%
Sinter acceleration agent aluminum group and amount	Al ₂ O ₃	0.50 wt%
Sinter acceleration agent of carbon group (dispersion medium) and amount	Cane sugar (water)	3.0wt%
Preliminary baking environment and temperature	Argon	800°C
Pressured sintering environment and temperature	Argon	2000°C
Sintering pressure and sintering time	500 kg/cm ²	10 min.
Average grain size of sintered body	5 ~ 10μ	
Apparent density of sintered body	3.18 g/cm ³	
pore ratio of sintered body	0 %	
Bending strength (at room temperature) of sintered body	56 kg/cm ²	
Polymorphism	6H>4H>15R	

(note) The amount of the additives are given with respect to the weight of silicon carbide fine powder. Also, cane sugar is the same as used in example 2.

Electron beam x-ray microanalysis of the sintered body did not show any segregation of boron and aluminum.

Example 4.

We removed the particles of grain size of more than 1μ from "black" powder of industrial silicon carbide by the sedimentation method. We obtained fine powder from the suspension by using a centrifuge. We treated it with nitric acid fluoride and obtained fine powder of specific surface area 8 m²/g. The amount of oxygen in this fine powder was 0.24 wt%. Results of other analyses were almost the same as those given in example 2.

We added to this fine boron powder of 0.15 wt% a condensed body

of 2.5 wt% furfuryl alcohol and formaldehyde polyvinylbutyl (combiner) of 3.wt%, and acetone (dispersive medium) of 40 wt%. We mixed it in a ball mill mixer made of polyethylene, dried it to obtain a fine powder for cool shaping. We rubber-pressed this powder and obtained a cylinder (about 10 x 10) of weight equivalent to 42g silicon carbide. We placed this cylinder in a graphite container and gradually raised its temperature up to 400°C at the rate of 50°C/min in argon flow, in order to remove the combiner. Then, we raised the temperature to 2050°C at the rate of 200°C/min and held it at this temperature for 30 minutes. We obtained a sintered body of the pore ratio ~12%.

In this sintering process, the cylinder contracted by ~18%. However, the contraction was uniform and no cracks were found. The bending strength 30 kg/cm^2 at the room temperature. Distribution of boron, aluminum and boron in the sintered body were uniform, as segregation at the grain boundary was not found by x-ray micro analyzer.

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